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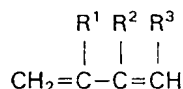
(71) Applicants
Imperial Chemical
Industries plc,
(Great Britain),
Imperial Chemical House,
Millbank,
London SW1P 3JF.

(72) Inventors
Manfred Bochmann

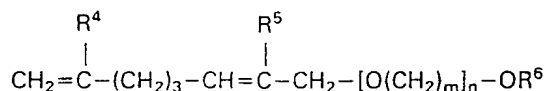
(74) Agents
Kenneth Stephenson,
Imperial Chemical
Industries plc,
Legal Department
Patents,
Thames House North,
Millbank,
London SW1P 4QG.

(54) Catalytic process for alkatrienyl ether derivatives

(57) A method for the preparation of unsaturated compounds containing at least 13 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R¹ and R², independently, represents hydrogen or alkyl and R³ represents hydrogen, alkyl or alkenyl, with a 1-substituted-2,7-alkadiene of the formula:



wherein each of R⁴ and R⁵ independently, represents hydrogen or alkyl, R⁶ represents hydrogen, a hydrocarbyl radical, an acyl radical or 1/z of an element, such as boron, aluminium or titanium, of valency z, m represents a whole number from 1 to 10 and n represents a whole number from 1 to 20, the reaction being carried out in the presence of a rhodium compound.

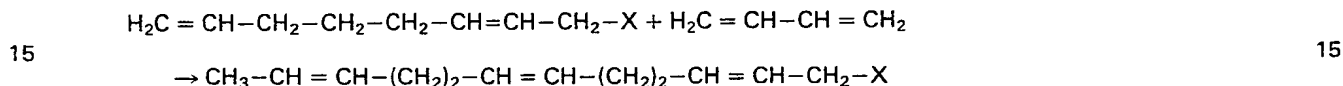
The products are useful intermediates in the manufacture of detergents.

SPECIFICATION

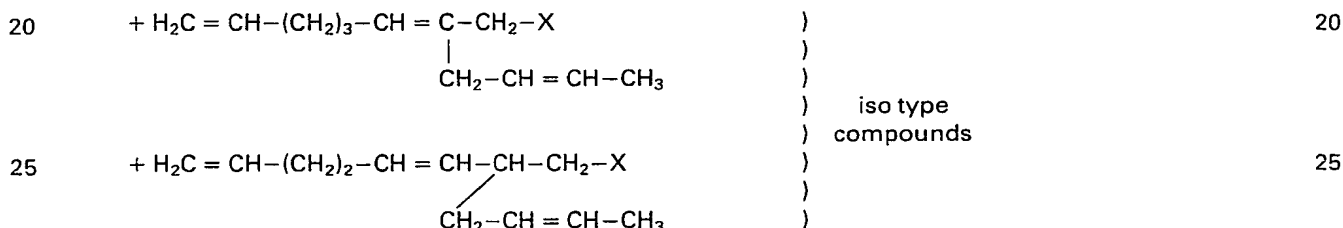
Chemical process

5 This invention relates to a chemical process and more particularly to a method for the preparation of certain unsaturated compounds. 5

It is already known from United Kingdom Patent Specification No. 1316725 to prepare unsaturated compounds having the structure of oligomers of butadiene by reacting a conjugated diene with a 1-substituted-2,7-alkadiene in the presence of a rhodium compound as catalyst. The reaction product 10 contains a mixture of a straight chain compound which has been referred to as a "normal type compound" and branched chain compounds which have been referred to as "iso type compounds". Thus, the reaction between 1,3-butadiene and a 1-substituted-2,7-octadiene may be represented as follows: 10



normal type compound



The ratio of normal type compound to iso type compounds will be referred to as the n/iso ratio.

30 The substituent X in the above compounds can be a hydroxy, alkoxy, aryloxy or acyloxy group. 30

The products of the reaction are useful chemical intermediates. In particular, the acyloxy substituted products may be converted by hydrolysis and hydrogenation into saturated higher alcohols useful in the manufacture of surfactant materials.

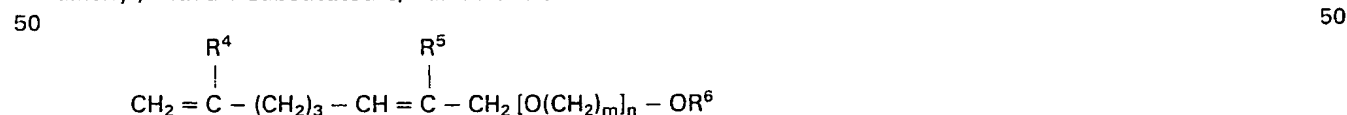
Methods for enhancing the activity of the rhodium catalyst have been proposed. Thus, Japanese Patent 35 Publication No. 75-13767 describes a process in which carbon tetrachloride or an alkylsilicon chloride is used in addition to the rhodium compound. According to Japanese Patent Publication No. 77-38533, the activity of this catalyst/co-catalyst system may be further improved by carrying out the reaction in the presence of hydrogen. 35

It has now been found that extremely useful products are obtained if the 1-substituted-2,7-octadiene used 40 in the reaction is a 1-hydroxyalkoxy-2,7-octadiene or a derivative thereof. 40

Thus, according to the invention, there is provided a method for the preparation of unsaturated compounds containing at least 13 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R¹ and R², independently, represents hydrogen or alkyl and R³ represents hydrogen, alkyl or alkenyl, with a 1-substituted-2,7-alkadiene of the formula:



55 wherein each of R⁴ and R⁵ independently, represents hydrogen or alkyl, R⁶ represents hydrogen, a hydrocarbyl radical, an acyl radical or 1/2 of an element, such as boron, aluminium or titanium, of valency z, m represents a whole number from 1 to 10 and n represents a whole number from 1 to 20, the reaction being carried out in the presence of a rhodium compound. 55

The alkyl radicals which may be represented by R¹ to R⁵ are preferably lower alkyl (C₁-C₄) radicals. Alkenyl radicals which may be represented by R³ preferably contain from two to four carbon atoms. Hydrocarbyl radicals which may be represented by R⁶ include alkyl, aralkyl, cycloalkyl and aryl radicals. Acyl radicals which may be represented by R⁶ include alkanoyl radicals, for example acetyl and propionyl and aroyl radicals, for example, benzoyl. 60

The number represented by m is preferably in the range 2 to 6, especially 2, and the number represented 65 by n is preferably 1 or 2 with especial preference for 1. 65

As examples of 1,3-dienes which may be used in the method of the invention, there may be mentioned isoprene, piperylene, 1,3,7-octatriene and especially 1,3-butadiene.

Substituted alkadienes for use in the method of the invention may be prepared by methods that have been fully described in the prior art. A particularly preferred material for use in the method of the invention is

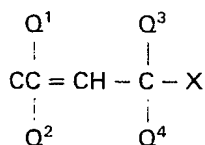
5 1-(2'-hydroxyethoxy)-2,7-octadiene.

The rhodium compound employed in the method of the invention may be an inorganic or organic salt or an organic complex. Examples of such compounds include rhodium trichloride, rhodium tribromide, rhodium nitrate, rhodium acetate, tetrakis(π -allyl)dichlorodirrhodium, tetrakis(ethylene)dichlorodirrhodium, bis(cycloocta-1,5-diene)dichlorodirrhodium and bis(π -crotyl)tetrachloro(butadiene)dirrhodium. The preferred catalyst is rhodium trichloride. The rhodium compound may be added directly to the other components of the reaction mixture but is preferably used in the form of a solution in an alcohol such as ethanol or in a hydrocarbon such as toluene. Suitable amounts of rhodium compound are in the range 10^{-5} to 10^{-1} gram-atom rhodium per mole of alkadiene.

It is advantageous to carry out the reaction in the presence of a promoter. Suitably promoters include organic halides and chromium compounds which may be used separately or in combination, optionally in the presence of hydrogen which enhances the effect of such promoters.

Organic halides which may be used as promoters include alkenyl, aralkyl, alkoxymethyl and, provided the substituted alkadiene is free from hydroxy groups, acyl halides.

Suitable alkenyl halides include, in particular, compounds of the formula:



wherein each of Q^1 , Q^2 , Q^3 and Q^4 , independently, represents hydrogen, alkyl (especially lower alkyl), alkenyl or aryl and X is chlorine or bromine. Examples of suitable alkenyl halides include allyl chloride, allyl bromide, crotyl chloride, crotyl bromide, 1-chloro-2,7-octadiene, 3-chloro-1,7-octadiene and cinnamyl chloride.

Suitable aralkyl halides include benzyl chloride, benzyl bromide and α,α,α -trichlorotoluene.

Suitable alkoxymethyl halides include chloromethyl methyl ether.

Suitable acyl halides for use when the alkadiene contains no hydroxy groups include compounds of the formula:



wherein Q^5 represents an optionally substituted alkyl, alkoxy, alkenyl or aryl radical (especially lower alkyl, lower alkoxy, lower alkenyl or phenyl) and X is chlorine or bromine. Examples of suitable acyl halides of this type include acetyl chloride, chloroacetyl chloride, dichloroacetyl chloride, trichloroacetyl chloride, methyl chloroformate, acryloyl chloride, cinnamoyl chloride and benzoyl chloride. Other suitable acyl halides include cyanuric chloride and compounds of the formula:



wherein Q^6 represents an optionally substituted alkyl or aryl radical and X is chlorine or bromine.

A particularly preferred organic halide for use as a promoter in the method of the invention is crotyl chloride.

The organic halide is suitably used in an amount of from 10 to 10^5 moles, preferably from 10^2 to 10^4 moles, per gram-atom of rhodium.

Chromium compounds which may be used as promoters include inorganic chromium salts such as chromic chloride which may be anhydrous or hydrated.

Hydrogen may be used with the above promoters by carrying out the reaction under a hydrogen pressure of 0.1 to 100 atmospheres, preferably 10 to 15 atmospheres.

The method of the invention may be performed by carrying out the reaction in a suitable reactor, for example an autoclave, at a temperature in the range 20-200°C, preferably 100-150°C. The reaction may take place under autogenous pressure, and the reactants may be used in bulk or in the form of solutions in suitable solvents.

The products obtained by the method of the invention are useful as chemical intermediates. In particular those products which contain a hydroxyalkoxy group are useful in the manufacture of detergents and other surfactant materials.

The invention is illustrated but not limited by the following Examples:

Example 1

Liquefied 1,3-butadiene (9 ml, ca. 100 mmol) was added at -20°C to 8.42g (49.5 mmol) 1-(2'-

hydroxyethoxy)-2,7-octadiene, 0.82g n-decane (g.l.c. standard), 4.53g (20 mmol) crotyl chloride, 0.5g

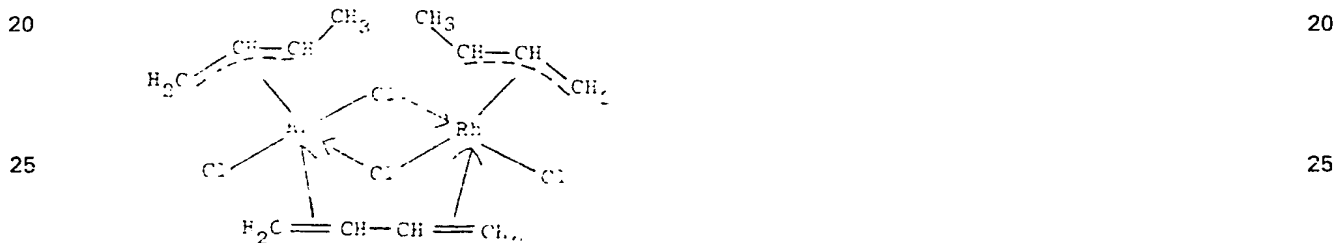
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.005 mmol Complex A (≈ 0.01 mg-atom Rh) in 1.0 ml toluene. The mixture was heated for 2 hours at 120°C in a glass-lined autoclave under hydrogen of 150 psi initial pressure and stirred magnetically. G.l.c. analysis after venting showed that 33% of the octadiene was converted to "normal type" and "iso type" compounds in 84% selectivity and an n/iso ratio of 0.3.

- 5 The lower boiling "iso type" compound can be separated from the "normal type" compound by preparative g.l.c. and consists of a mixture of two isomers analogous to the two isomers of 2-butenyl-octadienyl acetate described in GB 1,316,725.

The infra-red spectrum of the "iso-type" compound shows the following characteristic absorptions (in cm^{-1}): 3400 ($-\text{OH}$), 1635 ($-\text{C}=\text{C}-$), 1110 ($-\text{C}-\text{O}-$), 990 and 910 ($\text{H}_2\text{C}=\text{C}-$) and 965 (trans $-\text{CH}=\text{CH}-$). Both 10 isomers give virtually identical mass spectra. Characteristic peaks are m/e 224 (M^+), 169 ($\text{M}^+ - \text{C}_4\text{H}_7$), 162 ($\text{M}^+ - \text{HOC}_2\text{H}_4\text{OH}$), 147 ($\text{C}_{12}\text{H}_{18}^+ - \text{CH}_3$), 121 ($\text{C}_{12}\text{H}_{18}^+ - \text{C}_3\text{H}_5$), 107 ($\text{C}_{12}\text{H}_{18}^+ - \text{C}_4\text{H}_7$) and peaks resulting from successive loss of CH_2 and of butadiene. The spectrum proves the molecular weight and indicates the presence of an allyl- as well as a butenyl group in the structure of the compound.

The ^1H .m.r. spectra of the "normal type" compound and of the two isomers of the "iso type" compound 15 show great similarities to the reported spectra of the analogous dodecatrienyl acetates (Y Morita et al., Nippon Kagaku Zasshi 1971, 92, 853). Assignments were made on that basis. The $-\text{OCH}_2\text{CH}_2\text{OH}$ groups give rise to a multiplet at δ 3.5, $-\text{OH}$ appears at δ 2.8 (singlet).

Complex A has the structure:



30 Example 2

To 3.53g (20.7 mmol) 1-(2'-hydroxyethoxy)-2,7-octadiene in a strong-walled glass tube equipped with a pressure resistant Teflon valve were added 2.0 ml of a solution of 0.01 mmol Complex A in toluene and 0.38 g n-decane (g.l.c. standard). The mixture was cooled to -20°C and 1,3-butadiene (4 ml) was condensed in. The tube was sealed and heated on an oil bath at 110°C for 2 hours with magnetic stirring.

- 35 G.l.c. analysis showed an octadiene conversion of 22%, a selectivity to hydroxyethoxydodecatriene isomers of 96% and an n/iso ratio of 1.0.

Example 3

The same method as in Example 2 was followed for reacting 1-(2'-hydroxyethoxy)-2,7-octadiene with 40 1,3-butadiene (3 ml) in the presence of 0.1 mmol RhCl_3 , 0.5 ml ethanol and 20 mmol of an organic halide for 1 hour at 110°C . The results are collected in Table 1.

TABLE 1

45	Run No.	$\text{C}_8\text{H}_{13}\text{OC}_2\text{H}_4\text{OH}$ mmol	Organic halide	Conversion %	Sel %	n/iso ratio	45
	1	20.75	CCl_4	37	100	0.4	
50	2	20.6	$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$	59	100	0.4	50
	3	20.6	$\text{Ph}-\text{CH}=\text{CHCH}_2\text{Cl}$	97	99	0.4	

55 Example 4

The same method as in Example 2 was followed for reacting 3.53g 1-(2'-hydroxyethoxy)-2,7-octadiene with 1,3-butadiene (3.5 ml) in the presence of 0.01 mmol Complex A in 2.0 ml toluene and 1.89g (20 mmol) methyl chloroformate at 110°C for 2 hours. The conversion was 47%, the n/iso ratio 0.4

60 Example 5

The same method as in Example 2 was followed for reacting 8.48g (49.8 mmol) 1-(2'-hydroxyethoxy)-2,7-octadiene with 1,3-butadiene (9 ml) in the presence of 4.53g (50 mmol) crotyl chloride, 0.5g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.005 mmol Complex A in 1.0 ml toluene. After 2 hours at 110°C , the conversion was 21%, the selectivity 90% and the n/iso ratio 0.3.

Example 6

The same method as in Example 1 was followed for reacting 1-(2'-hydroxyethoxy)-2,7-octadiene with 1,3-butadiene (9 ml) in the presence of 0.005 mmol Complex A in 1.0 ml toluene and 4.53g (50 mmol) crotyl chloride under 150 psi hydrogen for 2 hours at various temperatures. The results are collected in Table 2.

Example 7

The same method as in Example 2 was followed for reacting 5.13g (24.1 mmol) 1-(2'-acetoxyethoxy)-2,7-octadiene with 1,3-butadiene (5 ml) in the presence of 2.8g (31 mmol) crotyl chloride and 0.01 mmol RhCl₃ in 1.0 ml ethanol. After 2½ hours at 110°C, the conversion was 72.5%, the selectivity to C₁₆ products 86% and the n/iso ratio 0.4.

Example 8

Tris [2'-(octa-2,7-dien-1-oxy)-ethoxy] aluminium, prepared from 21 mmol 1-(2'-hydroxyethoxy)-2,7-octadiene and 7 mmol triethyl aluminium, was reacted with 1,3-butadiene (3 ml), in the presence of 0.01 mmol Complex A in 2.0 ml toluene and 2.52g (16.5 mmol) cinnamyl chloride, following the same procedure as in Example 1. After 1 hour at 110°C and subsequent hydrolysis, the conversion was ca. 50%, the selectivity to C₁₄ products 100% and the n/iso ratio 0.4.

TABLE 2

Run No.	C ₈ H ₁₃ OC ₂ H ₄ OH mmol	Temperature °C	Conversion %	Sel. %	n/iso ratio
1	49.9	120	29	93	0.5
2	50.0	140	38	89	0.6

Example 9

The same method as in Example 2 was followed for reacting 4.51g (24.5 mmol) 1-(2'-methoxyethoxy)-2,7-octadiene with 1,3-butadiene (5 ml) in the presence of 1.96 (25 mmol) acetyl chloride and 0.005 mmol Complex A in 1.0 ml toluene. After 2 hours at 110°C, the conversion was 24%, the selectivity to C₁₅ products 100% and the n/iso ratio 0.5.

Example 10

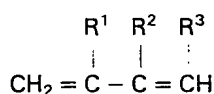
The same method as in Example 2 was followed for reacting 3.4g (18.4 mmol) 1-(3'-hydroxypropoxy)-2,7-octadiene with 1,3-butadiene (4 ml) in the presence of 1.81g (20 mmol) crotyl chloride and 0.005 mmol Complex A in 1.0 ml toluene for 2¼ hours at 110°C. The conversion of octadiene was 32%, the selectivity to C₁₅ products 92% and the n/iso ratio 0.5

Example 11

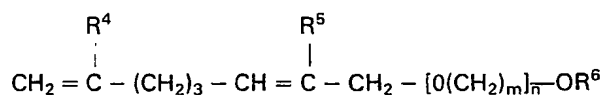
The same method as in Example 2 was followed for reacting 3.67g (18.5 mmol) 1-(4'-hydroxybutoxy)-2,7-octadiene with 1,3-butadiene (4 ml) in the presence of 0.005 mmol Complex A in 1.0 ml toluene and 1.81g (20 mmol) crotyl chloride for 2¼ hours at 110°C. The conversion was 95%, the selectivity to C₁₆ products 74% and the n/iso ratio 0.6.

CLAIMS (Filed on 11 Oct. 1982)

1. A method for the preparation of unsaturated compounds containing at least 13 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R¹ and R², independently, represents hydrogen or alkyl and R³ represents hydrogen, alkyl or alkenyl, with a 1-substituted-2,7-alkadiene of the formula:



wherein each of R⁴ and R⁵ independently, represents hydrogen or alkyl, R⁶ represents hydrogen, a hydrocarbyl radical, an acyl radical or ½ of an element, such as boron, aluminium or titanium, of valency z, m represents a whole number from 1 to 10 and n represents a whole number from 1 to 20, the reaction being

carried out in the presence of a rhodium compound.

2. A method according to claim 1 substantially as hereinbefore described with reference to the foregoing Examples.